

New Bond-Delocalized Dianions: The Crystal Structure of 1, 3-Bis(dicyanomethylene) Croconate Salt ($C_{11}N_4O_3K_2 \cdot 2H_2O$)

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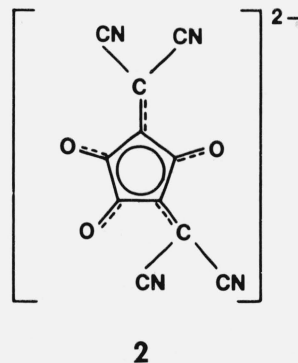
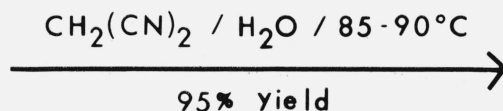
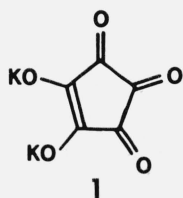
$C_{11}N_4O_3K_2 \cdot 2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a=8.568(2)$, $b=9.105(4)$, $c=9.818(4)\text{\AA}$, $\alpha=103.61(3)$, $\beta=107.63(3)$, $\gamma=101.58(3)^\circ$; $Z=2$, $\rho_{\text{calc}}=1.716$, $\rho_{\text{obs}}=1.72(2)\text{g cm}^{-3}$ (floatation). The structure was solved by direct methods and was refined by full-matrix least-squares procedures to a final R of 0.074 for 1989 observed reflections. The five-membered ring is planar and pentagonal. The two $=C(CN)_2$ groups define separate planes which form angles of 3.36 and 6.30° with the plane of the five-membered ring. The dianions form stacks along the a -axis. In a given stack, there is an alternating sequence of perpendicular distances (3.32 , 3.42\AA) between the planes defined by the ring atoms.

Key words: Bond delocalized dianion; oxocarbon; single-crystal; structure refinement; x-ray diffraction.

1. Introduction

Recently, the synthesis, properties and electronic structure of the dipotassium salt of 1,3-bis(dicyanomethylene)-2-oxo-4-cyclopentene-4,5-diol, a new analog of the croconate dianion, have been reported [1,2].¹ Treatment of dipotas-

sium croconate 1 with a one to two molar excess of malononitrile in aqueous solution at $85-90^\circ\text{C}$ yields the dipotassium salt of 2 as the dihydrate.



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¹ Figures in brackets indicate literature references located at the end of this paper.

Based on spectral analyses, the dianion 2 was assigned a planar, symmetrical bond-delocalized structure; hence, the dianion 2 may be regarded as a member of a new class of aromatic pseudo-oxocarbons with the formula $[C_5O_3X_2]^{2-}$ where $X = C(CN)_2$. In view of the fact that pseudo-oxocarbons constitute a new direction in the chemistry of aromatic oxocarbons [3,4], an x-ray analysis of the hydrated potassium salt of 2 was carried out. X-ray structural data are required to ascertain the degree of planarity and aromaticity of the dianion, to compare the molecular geometry of 2 with the corresponding parent oxocarbon, $[C_5O_3]^{2-}$, and to correlate the structure with chemical properties.

2. Experimental procedure

2.1 Crystal data and intensity data collection

Deep blue metallic needles suitable for x-ray analysis were obtained by recrystallization from water. A crystal was mounted on an automated single-crystal diffractometer and unit cell parameters were determined. The cell was reduced and an analysis of the reduced form showed that the symmetry is triclinic [5]. The reduction procedure is a mathematical procedure that guarantees that the cell edges are the three shortest possible translations ($a \leq b \leq c$) within the triclinic lattice for this material. As shown later in the discussion section, the a-axis coincides with the most impor-

tant structural feature. An examination of the NBS Crystal Data File (a magnetic tape file containing cell dimensions in reduced form of 60,000 materials; to be published) showed that 2 or a structurally related material has not been previously studied by x-ray diffraction. A full set of diffraction data was then collected. During the course of the diffraction experiment, three standard reflections were measured periodically and they showed a gradual net loss of intensity of approximately 5 percent. The intensity data were corrected for the drop of intensity observed in the standard reflections. A summary of the crystal data and the experimental conditions is given in table 1.

2.2 Structure solution and refinement

The structure was solved by direct methods. The model (all atoms except the water hydrogen atoms) was refined first by isotropic and then by anisotropic least-squares analysis. The thermal motion for all atoms appeared normal and indicated that the structure is tightly held together. The structure was refined to a conventional R of 0.074 for 1989 observed reflections. Examination of the final difference map revealed four peaks that could be interpreted as the water hydrogen atoms.

Although the model and the refinement are basically correct, there remain several abnormalities: 1) the R -value is too high in comparison with other crystal structure deter-

TABLE 1. Summary of crystal data and experimental conditions.

molecular formula	$K_2C_{11}N_4O_3 \cdot 2H_2O$
space group	P1
lattice constants ^a	$a = 8.568(2) \text{ \AA}$ $\alpha = 103.61(3)^\circ$ $b = 9.105(4)$ $\beta = 107.63(3)$ $c = 9.818(4)$ $\gamma = 101.58(3)$ $Z = 2$
density	$\rho(\text{calcd}) = 1.716 \text{ g cm}^{-3}$ $\rho(\text{obsd}) = 1.72(2) \text{ g cm}^{-3}$ (by flotation)
elemental analysis ^b	% K = 22.10 (22.32) % C = 37.51 (37.71) % H = 1.25 (1.15) % N = 15.88 (15.99)
radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$)
monochromator	graphite
μ (linear absorption coefficient)	$\mu = 7.22 \text{ cm}^{-1}$
absorption correction	no correction made
diffractometer	four circle diffractometer, bisecting mode
derivation of integrated intensities from measurements	integrated step scan
number of unique reflections	2396 total (1989 observed, 388 unobserved)
2θ limits	$4.0\text{--}50.0^\circ$
agreement among equivalent reflections	$R = 0.024$, average deviation = 0.70 σ
unobserved reflection criterion	reflections for which $I < 3\sigma(I)$ were classified unobserved
criterion for $\sigma(I)$	$\sigma(I)^2 = \text{total counts} + 3.76 \times 10^{-4} (\text{total counts})^2$
criterion for $\sigma(F)$	$\sigma(F_o) = [F_o^2 + \sigma(I)/Lp]^{1/2} - F_o$

^a The lattice constants were determined by a least-squares refinement using 15 reflections with 2θ values ranging between $4\text{--}19^\circ$.

^b Values calculated for $K_2C_{11}N_4O_3 \cdot 2H_2O$ are given in parentheses.

minations carried out on our automated diffractometer; 2) the R -value (0.036) for the $0kl$ projection (down the stacking axis, see sec. 3, Discussion) is much lower than the R -values for the $hk0$ (0.074) and the $h0l$ (0.087) projections; 3) there are too many small peaks ($\text{all} < 1 \text{ e}\text{\AA}^{-3}$) in the difference map. It is planned to take data on a second crystal to determine whether these anomalies result from the way the data were collected or whether they arise from the nature of the refine-

ment model. To our knowledge, highly refined models on other croconates (table 5) have not yet been reported. This is unfortunate because better refinements are required to ascertain the details of the bonding in the five-membered ring. A summary of the solution of the structure is given in table 2. The final atomic and thermal parameters are listed in tables 3 and 4 with the atomic labeling denoted in figure 1.

TABLE 2. Summary of solution of structure.

programs and computer	XRAY ^a and MULTAN ^b on Univac 1108
atomic scattering factors	neutral atom scattering factors ^c
anomalous scattering ^d : atom, $\Delta f'$, $\Delta f''$	K, 0.179, 0.250
solution method	direct methods
extinction	no correction
weighting scheme	$w = 1/[\sigma(F_o)]^2$ for observed reflections $w = 0$ for unobserved reflections
refinement	full-matrix least-squares; refinement was based on minimization of $\Sigma w(F_o - F_c)^2$
R value (for 1989 observed reflections)	$R = \Sigma F_o - F_c / \Sigma F_o = 0.074$

^a J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, XRAY 76, Technical Report TR-446, Computer Science Center, University of Maryland, College Park, MD.

^b G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr., Sect. A, 27, 368 (1971).

^c For hydrogen, see R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., 42, 3175 (1965). For all other atoms, see D. T. Cromer and J. B. Mann, Acta Crystallogr., Sect. A, 24, 321 (1968).

^d International Tables for X-ray Crystallography, Vol. IV, (Kynoch Press, Birmingham, England, 1974) p. 149.

TABLE 3. List of atomic parameters ($\times 10^3$)^{a,b}.

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(1)	2197(7)	5055(6)	5745(5)	255(29)	241(26)	217(26)	108(23)	70(23)	86(21)
C(2)	3145(7)	5870(6)	5011(6)	252(31)	220(27)	238(27)	91(23)	52(24)	68(22)
C(3)	3006(6)	4734(6)	3633(5)	192(28)	205(26)	222(26)	48(21)	46(22)	58(21)
C(4)	1992(7)	3217(6)	3523(6)	232(30)	207(26)	275(28)	52(22)	49(24)	79(22)
C(5)	1529(7)	3404(6)	4868(6)	279(31)	241(27)	242(27)	91(24)	70(24)	100(22)
C(6)	1956(7)	5746(6)	7051(6)	257(30)	236(26)	276(27)	62(23)	100(24)	95(22)
C(7)	1051(8)	4863(6)	7732(6)	410(36)	308(29)	296(29)	117(26)	169(28)	107(24)
C(8)	2563(8)	7420(7)	7798(6)	321(34)	322(32)	303(29)	94(26)	183(26)	91(25)
C(9)	3736(7)	5064(6)	2611(6)	325(32)	188(26)	255(28)	52(23)	121(25)	43(21)
C(10)	3606(8)	3843(6)	1326(6)	394(36)	293(29)	297(30)	90(26)	149(27)	103(26)
C(11)	4642(8)	6606(6)	2752(6)	351(34)	308(31)	302(29)	102(26)	191(27)	79(24)
N(7)	341(8)	4221(6)	8326(6)	780(44)	437(32)	538(34)	166(30)	393(34)	221(28)
N(8)	2950(7)	8731(6)	8437(6)	522(36)	307(29)	460(29)	68(25)	282(27)	27(23)
N(10)	3530(8)	2870(6)	308(6)	619(39)	388(28)	381(28)	77(26)	265(28)	20(24)
N(11)	5390(8)	7830(6)	2801(6)	548(38)	301(27)	514(33)	-12(26)	307(30)	104(24)
O(2)	3970(5)	7302(4)	5496(4)	421(25)	211(20)	320(20)	32(18)	172(19)	64(16)
O(4)	1545(5)	1946(4)	2491(4)	430(25)	186(18)	265(20)	7(17)	89(18)	-17(16)
O(5)	685(5)	2313(4)	5140(4)	486(26)	248(20)	366(22)	24(18)	202(20)	117(17)
K(1)	9194(2)	9266(1)	2717(1)	447(9)	294(7)	328(8)	57(6)	145(6)	95(5)
K(2)	3739(2)	200(1)	1841(1)	365(8)	310(7)	380(8)	48(6)	146(6)	67(6)
O(W1)	2718(6)	-435(5)	4190(5)	599(33)	364(23)	465(25)	130(22)	119(24)	146(20)
O(W2)	578(6)	8226(5)	439(4)	479(28)	444(24)	354(22)	-75(21)	130(21)	92(19)

^aThe estimated standard deviations of the last significant digits are given in parentheses.

^bThe form of the thermal correction is: $T = \exp[-2\pi^2(a^2h^2U_{11} + b^2k^2U_{22} + c^2l^2U_{33} + 2a^*b^*hkU_{12} + 2a^*c^*hlU_{13} + 2b^*c^*klU_{23})]$.

TABLE 4. List of atomic parameters ($\times 10^3$) for hydrogen ^a.

atom	x	y	z
H(1) ^b	321	-133	438
H(2)	357	40	469
H(3)	-18	800	-59
H(4)	14	717	70

^a Positional parameters for the hydrogen atoms were deduced from a difference map, but were not refined.

^b Hydrogen atoms H(1) and H(2) are bonded to O(W1) while H(3) and H(4) are bonded to O(W2).

3. Discussion

3.1 The ring parameters

Bond distances, angles and thermal ellipsoids for the dianion are illustrated in figure 1. The x-ray data indicate that there is delocalization of the π electrons in the five-membered ring of 2 as in its croconate analogs. Various resonance forms for the dianion are shown in figure 2. The relative contribution of each resonance form to the ground state resonance hybrid may be responsible for the slight variations in the observed C=O and ring C-C bond lengths. The mean C=O and C-C bond lengths of 1.244(6) and 1.450(8) Å, respectively, agree with the corresponding values of 1.243 and 1.458 Å which have been calculated for

compounds of the form $[\text{C}_5\text{O}_5]^{2-}$ with planar, D_{5h} symmetry [6]. The five endocyclic angles are each within one estimated standard deviation of 108° , the theoretical value for a regular pentagon.

Table 5 provides a comparison of ring dimensions in 2 with several croconate salts and complexes. From a comparison of 2 with $(\text{NH}_4)_2\text{C}_5\text{O}_5$, it can be concluded that the electronic distribution in the five-membered ring in the former is approximately the same as in the unsubstituted croconate dianion. Thus, the two dicyanomethylene substituents do not appear to have significantly disturbed the ideal D_{5h} symmetry of the ring. The relatively wide range of values obtained for the endocyclic angles and C-C distances in the four remaining compounds indicates that, to varying degrees, there is some localization of the π electrons within the rings. In RbHC_5O_5 and $\text{NH}_4\text{HC}_5\text{O}_5$, the resonance in the monobasic croconate anion has been influenced by the presence of the hydroxyl hydrogen atom. In the five-membered ring of $\text{C}_5\text{O}_5\text{Cu}(\text{H}_2\text{O})_3$ and $\text{C}_5\text{O}_5\text{Zn}(\text{H}_2\text{O})_3$, the coordination of the croconate dianion to the transition metals has been found to affect the ring geometry. Nevertheless, for the dianions, the mean C-C bond distances in the various rings are very similar. Before detailed comparisons can be made, however, x-ray structure work of higher precision must be carried out because of the high estimated standard deviations on all the distances and angles listed in table 5.

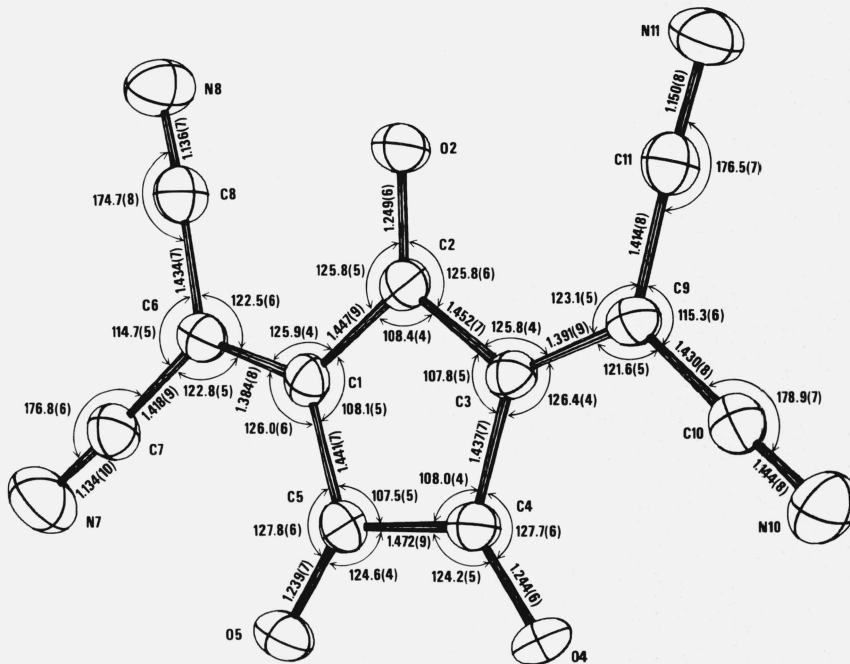


FIGURE 1. Bond distances (Å) and angles (°) for the dianion.

Thermal ellipsoids are drawn at the 50% level of probability [14].

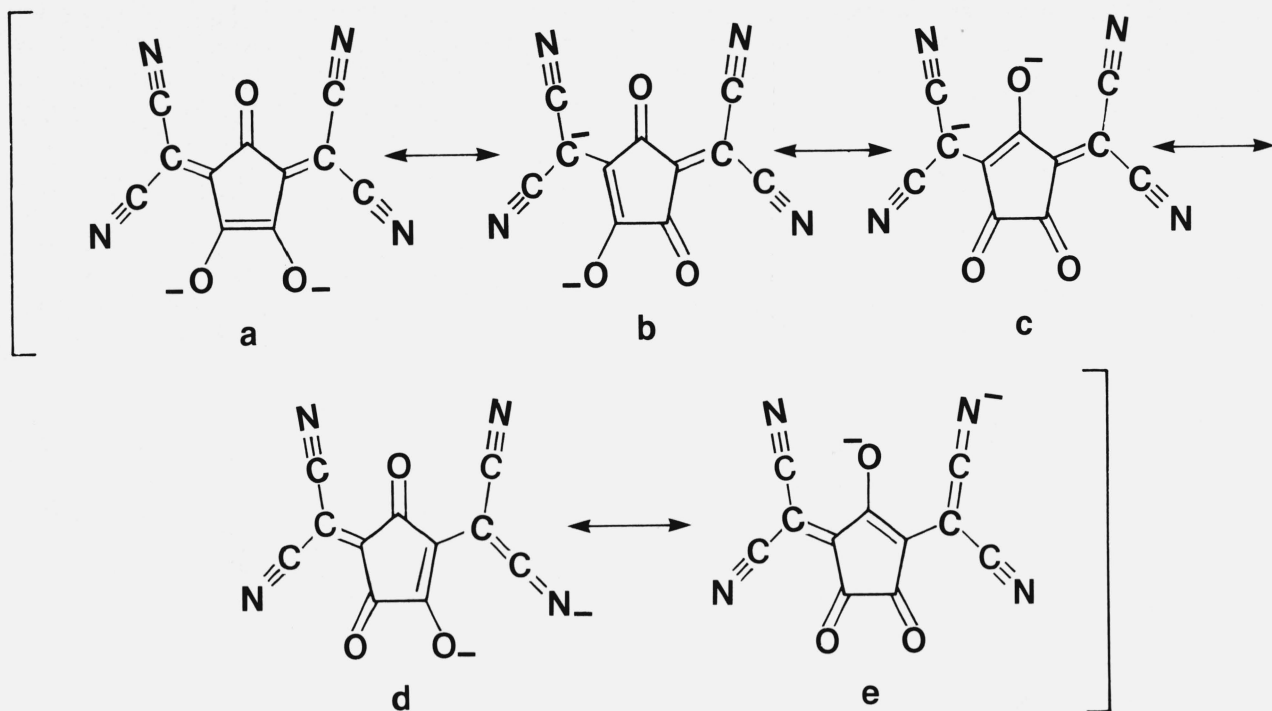


FIGURE 2. Five of several possible resonance forms for 2.

TABLE 5. Comparison of ring bond distances (Å) and angles (°) in several croconate compounds.

	$K_2C_{11}N_4O_3 \cdot 2H_2O$ ^a	$RbHC_5O_3$ ^b	$NH_4HC_5O_3$ ^b	$(NH_4)_2C_5O_3$ ^c	$C_5O_3Cu(H_2O)_3$ ^d	$C_5O_3Zn(H_2O)_3$ ^d
C(1)–C(2)	1.447(9)	1.54(2)	1.56(2)	1.452(10)	1.459(14)	1.484(17)
C(2)–C(3)	1.452(7)	1.40(6)	1.40(3)	1.452(10)	1.457(11)	1.480(13)
C(3)–C(4)	1.437(7)	1.45(4)	1.42(2)	1.463(13)	1.446(11)	1.415(18)
C(4)–C(5)	1.472(9)	1.47(6)	1.44(3)	1.455(18)	1.432(12)	1.475(16)
C(5)–C(1)	1.441(7)	1.54(5)	1.55(3)	1.463(13)	1.491(12)	1.501(16)
average	1.450(8)	1.48(5)	1.47(3)	1.457(13)	1.457(12)	1.471(16)
C(1)–O(1)	—	1.25(5)	1.24(2)	1.241(11)	1.240(10)	1.274(12)
C(2)–O(2)	1.249(6)	1.23(3)	1.21(2)	1.289(13)	1.249(11)	1.186(14)
C(3)–O(3)	—	1.34(4)	1.37(2)	1.241(11)	1.244(11)	1.247(13)
C(4)–O(4)	1.244(6)	1.27(6)	1.18(2)	1.269(11)	1.276(10)	1.254(12)
C(5)–O(5)	1.239(7)	1.21(2)	1.19(1)	1.269(11)	1.243(12)	1.217(17)
average	1.244(6)	1.26(4)	1.24(2)	1.262(11)	1.250(11)	1.236(14)
C(5)–C(1)–C(2)	108.1(5)	102(3)	106(2)	106.6(5)	108.6(7)	111.2(9)
C(1)–C(2)–C(3)	108.4(4)	108(3)	102(1)	110.0(7)	106.9(7)	103.8(9)
C(2)–C(3)–C(4)	107.8(5)	113(3)	118(2)	106.6(5)	108.3(7)	110.5(9)
C(3)–C(4)–C(5)	108.0(4)	106(5)	105(2)	108.4(6)	110.0(7)	110.8(9)
C(4)–C(5)–C(1)	107.5(5)	109(2)	108(1)	108.4(6)	106.1(7)	103(1)

^a This study.

^b N. C. Baenziger and D. G. Williams, *J. Am. Chem. Soc.*, **88**, 689 (1966).

^c N. C. Baenziger and J. J. Hegenbarth, *ibid.*, **86**, 3250 (1964).

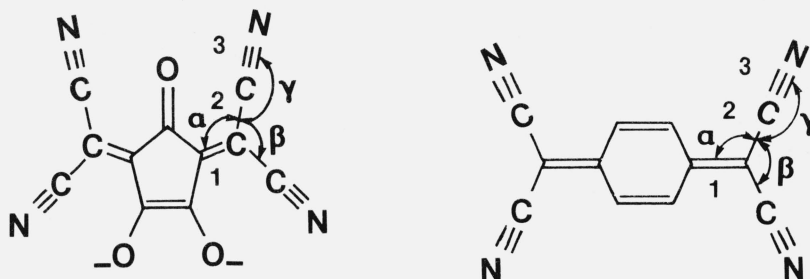
^d M. D. Glick, G. L. Downs, and L. F. Dahl, *Inorg. Chem.*, **3**, 1712 (1964).

3.2 The dicyanomethylene groups

A comparison of averaged bond distances and angles shows close agreement between the dicyanomethylene groups in **2**, TCNQ (7,7,8,8-tetracyanoquinodimethane), and several TCNQ complexes (table 6). The least-squares plane results given in table 7 reveal that although the five ring atoms lie in the same plane (average and maximum deviation from the plane being 0.012 and 0.018 Å, respectively), the dianion is not quite planar. The two dicyanomethylene

groups are rotated in the same direction about the exocyclic C—C bonds. The planes of the two dicyanomethylene groups form angles of 3.36° and 6.30° with the plane defined by the ring atoms. Similar twisting of the dicyanomethylene groups out of the plane of the ring has been observed in TCNQ and in the TCNQ moiety of complexes such as (TMTTF)_{1.3}(TCNQ)₂ and (DMBP)²⁺(TCNQ)₃²⁻ [7]. In **2**, however, the twisting pattern is more pronounced than in the TCNQ moieties of the aforementioned structures which may result from intramolecular steric repulsive forces in addition to the predominant effects of packing [8].

TABLE 6. Comparison of average bond distances (Å) and angles (°)^a.



	K ₂ C ₁₁ N ₄ O ₃ · 2H ₂ O ^b	(TMTTF) _{1.3} (TCNQ) ₂ ^c	TTF-TCNQ ^d	Chysene- TCNQ ^e	Pyrene- TCNQ ^f	TCNQ ^g
1.....	1.388(9)	1.387(10)	1.402(3)	1.386(7)	1.35(1)	1.374(3)
2.....	1.424(8)	1.437(10)	1.423(3)	1.428(9)	1.43(1)	1.440(4)
3.....	1.141(8)	1.142(11)	1.151(4)	1.139(10)	1.14(1)	1.140(3)
α.....	122.5(5)	122.4(6)	121.1(3)	122.2(5)	122.0(5)	121.9(2)
β.....	115.0(6)	115.2(6)	117.8(2)	115.6(5)	115.9(5)	116.1(2)
γ.....	176.7(7)	179.1(7)	177.1(2)	178.4(6)	178.4(7)	179.5(2)

^a For comparison, averaged bond distances and angles have been tabulated for the dicyanomethylene groups of the dipotassium salt of 1,3-bis(dicyanomethylene)-2-oxo-4-cyclopentene-4,5-diol, TCNQ, and several TCNQ-complexes. See table figures for labeling scheme.

^b This study.

^c T. J. Kistenmacher, T. E. Phillips, D. O. Cowan, J. P. Ferraris, A. N. Bloch, and T. O. Poehler, *Acta Crystallogr.*, Sect. B, 32, 539 (1976).

^d T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *ibid.*, Sect. B, 30, 763 (1974).

^e P. J. Munnoch and J. D. Wright, *J.C.S. Perkin II*, 1397 (1974).

^f C. K. Prout, I. J. Tickle, and J. D. Wright, *ibid.*, 528 (1973).

^g R. E. Long, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr.*, 18, 932 (1965).

TABLE 7. Least-squares plane analysis^a.

atom	delta	atom	delta
*C(1)	-0.017 Å	C(10)	0.084 Å
*C(2)	0.009	C(11)	-0.044
*C(3)	0.002	N(7)	-0.058
*C(4)	-0.013	N(8)	-0.355
*C(5)	0.018	N(10)	0.159
C(6)	-0.084	N(11)	-0.092
C(7)	-0.066	O(2)	0.056
C(8)	-0.212	O(4)	-0.054
C(9)	0.016	O(5)	0.042

^a Atoms used to define the plane are marked with asterisks.

3.3 The packing

The dianions are arranged in stacks parallel to the *a*-axis of the cell. The normal to the plane defined by the five-membered ring forms an angle of 38.2° with the *a*-axis. In a given stack (fig. 3), there is an alternating sequence of perpendicular distances (3.32, 3.42 Å) between the planes defined by the ring atoms. The magnitudes of these interplanar spacings are comparable to those found in many charge-transfer complexes [8]; for example, in crystals of TMTTF-bromoanil [9] and $(\text{TCNQ})_2\text{TMPD}^+$ [10] segregated stacks of donor and acceptor molecules are formed in which the interplanar spacings between acceptors were found to be 3.39 and 3.24 Å, respectively. The relative arrangement of the molecular stacks in 2 is such that the packing may also be viewed in terms of anionic layers (fig. 4) with interleaving potassium ions and water molecules. The coordination about each potassium ion and water molecule is illus-

trated in figures 5 to 8 while the pertinent distances are listed in table 8.

3.4 Potassium coordination

Each potassium ion is surrounded by four nitrogen atoms with $\text{K} \cdots \text{N}$ distances ranging between 3.007(7) and 3.293(7) Å for K(1) and 2.925(7) to 3.154(7) Å for K(2). Somewhat shorter $\text{K} \cdots \text{N}$ distances have been observed in K-TCNQ [11] with the values ranging between 2.873 and 2.976 Å, while somewhat longer $\text{K} \cdots \text{N}$ distances between 3.259(14) and 3.800(14) Å were found in potassium dinitrotrichlorocyclopentadienide [12]. K(1) is surrounded by five oxygen atoms at distances ranging between 2.803(5) and 2.936(4) Å whereas for K(2) there are four $\text{K} \cdots \text{O}$ interactions with the K(2) $\cdots \text{O}$ distances ranging between 2.662(5) and 2.857(4) Å. These $\text{K} \cdots \text{O}$ values are consistent with those reported for potassium dinitrotrichlorocyclopentadienide where distances between 2.580(12) and 2.942(11) Å were observed.

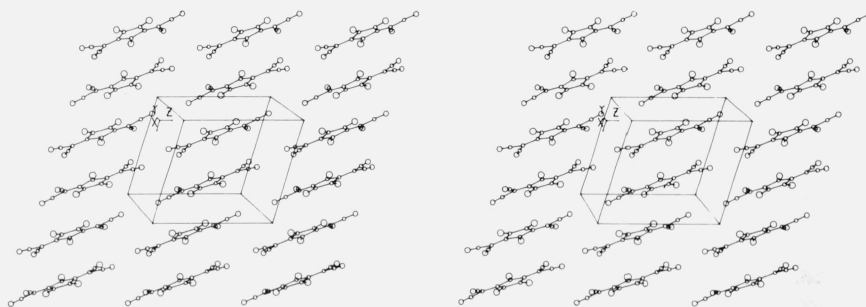


FIGURE 3. Stereoscopic view of the stacks formed by the dianions.

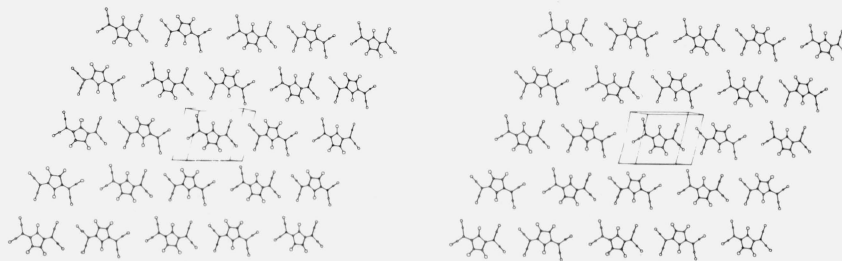


FIGURE 4. Stereoscopic view of the structure projected down the *a*-axis.

The molecules drawn were chosen to best illustrate the formation of the anionic layer.

TABLE 8. *Coordination (less than 3.5 Å) about the potassium ions and water molecules.*

K(1) ... O(W1) ^a	2.849(6)	O(W1) ... K(1) ^a	2.849(6)
K(1) ... O(W2) ^a	2.892(6)	O(W1) ... K(2)	2.840(6)
K(1) ... O(4) ^a	2.935(5)	O(W1) ... O(W2) ^d	3.364(6)
K(1) ... O(5) ^a	2.936(4)	O(W1) ... O(2) ^d	2.888(7)
K(1) ... O(5) ^m	2.803(5)	O(W1) ... O(2) ^m	3.478(7)
K(1) ... N(7) ^m	3.242(7)	O(W1) ... O(4)	3.171(7)
K(1) ... N(8) ^a	3.007(7)	O(W1) ... O(5)	3.435(7)
K(1) ... N(10) ^f	3.052(6)	O(W1) ... O(5) ^f	3.398(8)
K(1) ... N(11)	3.293(7)	O(W1) ... N(11) ^d	3.454(9)
		O(W1) ... N(11) ^m	3.040(6)
K(2) ... O(W1)	2.840(6)	O(W2) ... K(1) ^b	2.892(6)
K(2) ... O(W2) ^d	2.662(5)	O(W2) ... K(2) ^f	2.662(5)
K(2) ... O(2) ^m	2.857(4)	O(W2) ... O(W1) ^f	3.364(6)
K(2) ... O(4)	2.814(5)	O(W2) ... O(4) ^f	3.297(6)
K(2) ... N(8) ^f	3.095(6)	O(W2) ... O(4) ^f	2.848(6)
K(2) ... N(8) ^m	2.925(7)	O(W2) ... N(7) ^k	2.864(8)
K(2) ... N(10)	3.154(7)	O(W2) ... N(8) ^f	3.267(9)
K(2) ... N(11) ^d	2.986(6)	O(W2) ... N(10) ^f	3.257(8)

Symmetry codes:

(no symbol)	x,	y,	z
(a)	-1+x,	-1+y,	z
(b)	-1+x,	y,	z
(c)	x,	-1+y,	-1+z
(d)	x,	-1+y,	z
(e)	x,	y,	-1+z
(f)	x,	1+y,	z
(g)	1+x,	y,	z
(h)	1+x,	1+y,	z
(i)	-x,	-y,	1-z
(j)	-x,	1-y,	-z
(k)	-x,	1-y,	1-z
(l)	1-x,	1-y,	-z
(m)	1-x,	1-y,	1-z
(n)	1-x,	2-y,	1-z

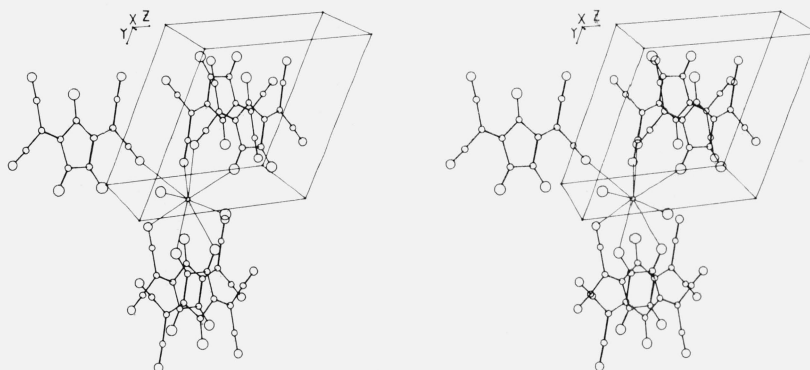


FIGURE 5. *Stereoscopic view of the coordination about K(1).*†

†The potassium ions are represented by small circles while the large circles represent the oxygen atom of a water molecule. The coordination distances and symmetry relationships are indicated in table 8.

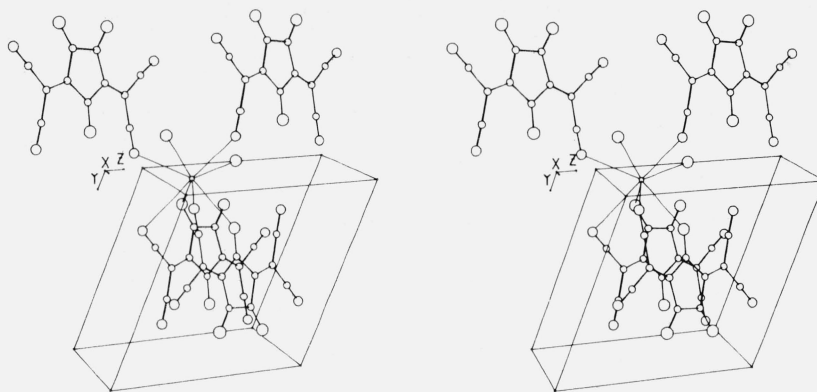


FIGURE 6. *Stereoscopic view of the coordination about K(2).†*

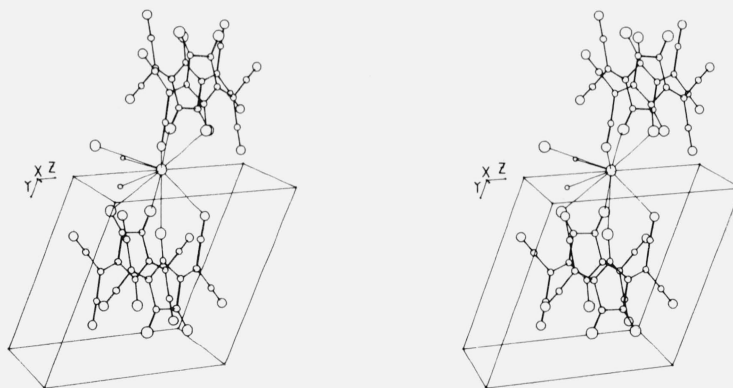


FIGURE 7. *Stereoscopic view of the coordination about O(W1).†*

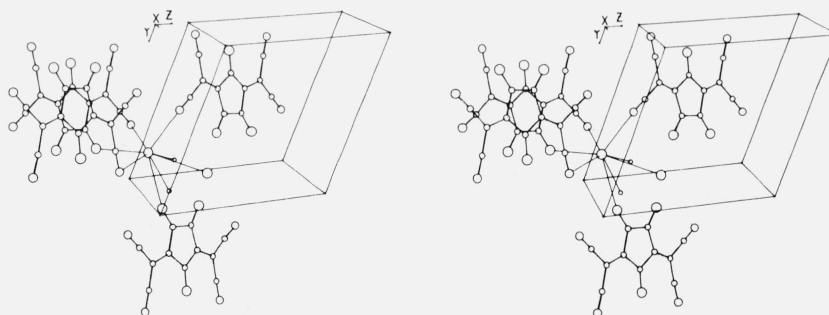


FIGURE 8. *Stereoscopic view of the coordination about O(W2).†*

†The potassium ions are represented by small circles while the large circles represent the oxygen atom of a water molecule. The coordination distances and symmetry relationships are indicated in table 8.

3.5 Water coordination

Both water molecules are irregularly surrounded by potassium ions and by nitrogen and oxygen atoms. From an analysis of the approximate hydrogen atom positions deduced from the final difference map, each water molecule was found to participate in weak hydrogen bonds to the nearest oxygen and nitrogen atoms. Although both water molecules are hydrogen bonded to dianions in adjacent stacks, O(W1) is hydrogen bonded to molecules in the same anionic layer while O(W2) is hydrogen bonded to dianions in different layers. The hydrogen-bond distances and angles are summarized in table 9. The HOH angles were found to be 104° for O(W1) and 103° for O(W2).

TABLE 9. Hydrogen-bond distances (Å) and angles (°).

$A-H \cdots B-C$	d_{A-H}	$d_{H \cdots B}$	$d_{A \cdots B}$	$\angle A-H \cdots B$
O(W1)-H(1) ... O(2) ^a	1.02 †	1.93	2.888(7)	156
O(W1)-H(2) ... N(11) ^b	0.86	2.39	3.040(6)	133
O(W2)-H(3) ... O(4) ^c	0.97	1.89	2.848(6)	167
O(W2)-H(4) ... N(7) ^d	1.08	1.81	2.864(8)	164

Symmetry codes:

(a)	x,	-1+y,	z
(b)	1-x,	1-y,	1-z
(c)	-x,	1-y,	-z
(d)	-x,	1-y,	1-z

† Estimated standard deviations are omitted since the hydrogen atom positions were not refined.

4. Conclusion

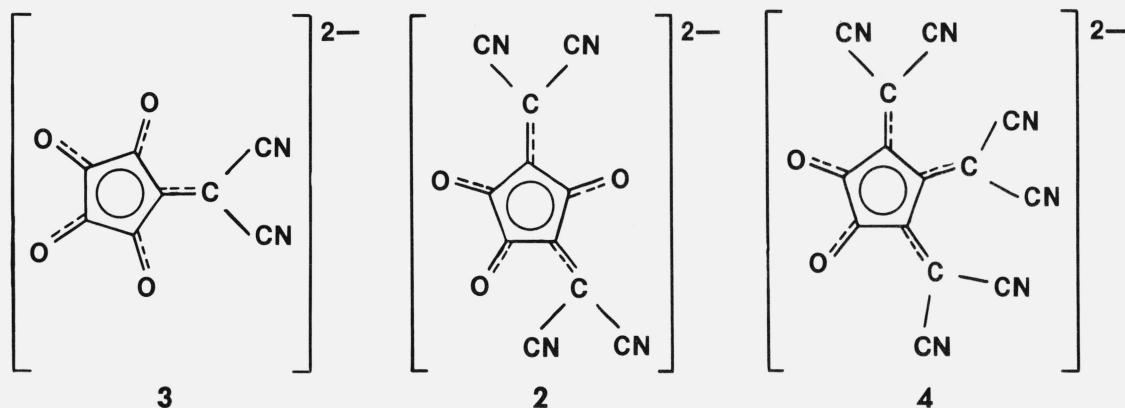
This structural study reveals a close relationship (with respect to ring planarity and parameters) between the oxocarbon $[C_5O_5]^{2-}$ and 2. Thus, the x-ray evidence verifies that

2 can be viewed as a pseudo-oxocarbon with a formula $[C_5O_3X_2]^{2-}$ where $X = C(CN)_2$. On the basis of this study, it is predicted that the ring parameters of pseudo-oxocarbons of the type $[C_5O_4X]^{2-}$, 3, and $[C_5O_2X_3]^{2-}$, 4, would also be similar to 2 and to the parent oxocarbon. To verify or disprove this prediction, x-ray work will be carried out on 3 and 4 if suitable crystals can be prepared. In 4, the three adjacent dicyanomethylene groups must rotate (about the exocyclic C—C bonds) with respect to the plane of the ring due to the proximity of these substituents. It is likely, however, that the ring distances and angles will not be altered significantly by this rotation because the ring atoms and the atoms attached to the ring can remain coplanar. Also, work is contemplated on pseudo-oxocarbons in the squarate series $[C_4O_4]^{2-}$ in which specific carbonyl oxygen atoms have been replaced by dicyanomethylene groups. The dianion $[C_4O_2X_2]^{2-}$ will be studied to compare the ring distances and angles with the parent compound whose structure has been determined [13]. This will make possible a comparison of the oxocarbons and pseudo-oxocarbons within and between the four- and five-membered ring series.

In certain respects, the packing in 2 resembles that of TCNQ and its myriad complexes in that stacks are formed with short interplanar distances. It seems likely that a great variety of materials with unusual physical properties can be prepared by combining various pseudo-oxocarbons with appropriate cations.

5. References

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